

# RELATIONSHIP BETWEEN IRON ORE DEPOSITS AND SPREAD OF HEAVY METALS IN SHALLOW WATER RIVERS: NATURAL AND MAN-CAUSED FACTORS

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### Key words:

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## ABSTRACT

This paper describes the results of a study that looked at the effect of natural and human factors related to iron ore deposits on the distribution of heavy metals. A case study of one of the low-water rivers situated in the area of the Kursk-Belgorod Magnetic Anomaly is considered. The study looked at the Oskol river, a typical low-water stream largely susceptible to heavy metal pollution. With the current mining, transportation and waste storage techniques, HMs spread over vast territories carried with dust and waste waters and thus pollute rivers, which in fact accumulate the contaminants. The paper describes the results of zoning of the low-water Oskol river, which is under the impact of various factors caused by iron ore deposits. The zoning was done based on the natural and technogenic features. The research was carried out based on the authors' method. Hydrochemical anomalies were determined based on 'Reference Hydrochemical Background', which is formed on the basis of both natural and human factors. Concentrations of heavy metals significantly increase in the zone of direct impact of mining and steel companies and single-industry cities. This indicates a significant impact of man-caused pollution. The research showed that the low-water Oskol river is highly susceptible and has a low self-purification ability. Heavy metal pollution affects the terrestrial and aquatic ecosystems, ultimately affecting the quality of life and public health. The cropout of ferruginous quartzites with a high iron content, numerous mining and steel sites located in the river basin, the spread of heavy metals with air currents and surface waters over long distances — all this is causing a large-scale pollution. Because of this we cannot expect any real improvement in the next few years.

## 1. Introduction.

Iron ore deposits can affect the environment in many ways. There can be different sources of pollution. First of all, when ferruginous quartzites crop out, get weathered, washed or carried over long distances, the concentration of iron ions rises. Secondly, mining and processing of iron ores are associated with the growth of mining and steel industries, as well as single-industry cities. The latter add to the pollution. Degradation — both in terms of changing chemical composition and depletion — of rivers, lakes and other surface waters caused by iron ore deposits is almost inevitable. This problem is especially acute in traditional industrial areas with low waters.

Iron ore deposits contribute to the creation of a hydrochemical anomaly characterized with a combination of hazardous chemical substances and elements. Heavy metals (HMs) constitute one of the classes of such pollutants. Pollution may lead to hydrochemical changes, formation of toxic components and degradation of minor rivers. Heavy metals generated in the areas impacted by iron ore deposits are extremely harmful for aquatic ecosystems, and this fact, combined with the susceptibility of minor rivers, stresses the relevance of our research. Considering the subject, our research can be subsumed under the category: “Sustainable use of natural resour-

ces”, one of the priority areas in Russia's science and technology.

The aim of this research is to study the natural and human factors behind the spread of heavy metals caused by iron ore deposits by considering the case study of one of the low-water rivers in the Kursk-Belgorod Magnetic Anomaly.

The following tasks have been accomplished to achieve the above aim:

1. To understand the heavy metals distribution patterns accounting for natural and human factors.
2. To do zoning of the Oskol river on the basis of its natural features and human impact.
3. To understand the seasonal and spatial distribution of HMs in the Oskol river waters caused by iron ore deposits.
4. To describe the impact of HMs on minor rivers.

The problem of environmental pollution caused by mining and steel industries has long been a point of concern for both Russian and foreign researchers. The authors of the list of complex issues faced by Russian steel and mining industries point out, among other things, the inevitability of environmental pollution [1]. The authors are in complete accord with the statement that the introduction of the most advanced technology in Russia's ferrous metallurgy would be consistent with environmental protection [2–4].

## 2. Materials and Methods of Research

The object of study included the Oskol river. The river and its tributaries are of great importance for the region, and the Oskol can be regarded as a low-water river. The following industrial sites are situated in the river basin: Oskol Electrometallurgical Steel Works (OEMK), Lebedinsky GOK (LGOK), Stoilensky GOK (SGOK) and other mining and steel companies. The presence of numerous mining and steel companies in the river basin is due to the fact that the river flows through the Kursk-Belgorod Magnetic Anomaly. The river basin also houses the single-industry cities of Gubkin and Staryi Oskol, with the mining companies and steel makers being the main employers for the local population. Our findings, which are consistent with the conclusions made by other researchers, show that the river basin has been under tremendous human impact for many years [5–7].

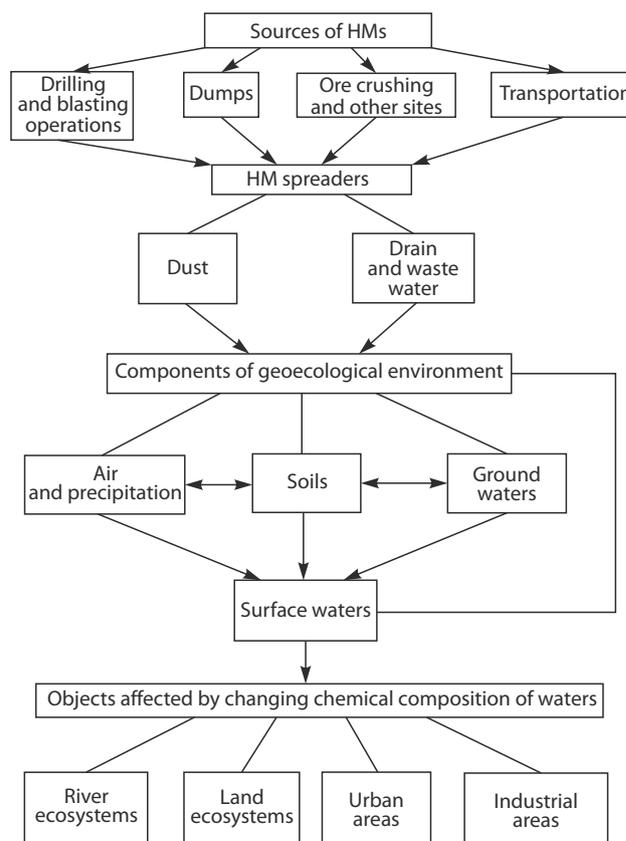
This study has been carried out on the basis of an original method used by the authors for studying complex objects. The method comprises a few successive stages. The first stage includes zoning of the Oskol river on the basis of its natural features, as well as the impact produced by mining and steel making companies. The second stage involves looking at the concentrations of heavy metals using the hydrochemical analysis data from certain sampling points on the Oskol river. The third stage involves a summary of spatial and seasonal variations in the HM concentrations based on natural and human factors.

The hydrochemical characteristic of the Oskol river is based on the water quality data obtained through the hydrometeorological stations of the Belgorod Region, as well as from the State Water Resources Control Board. Seasonal and mean annual data on water quality from the 2018 samples were analyzed to understand when heavy metals got in the water and how they spread. By comparing the quality of water sampled from different sections of the river during different seasons, we will be able to understand the hydrochemical processes taking place in low-water rivers and analyse the spatial and seasonal dynamics of heavy metals. Maximum allowable concentrations of hazardous substances applicable to freshwater ponds and fisheries were used as the criteria for heavy metals pollution of low-water rivers.

Hydrochemical anomalies were identified based on a ‘Reference Hydrochemical Background’ specified by the authors, which is attributable to both natural and human factors. To define the reference background limits, variation limits were calculated for the hydrochemical components with a given confidence probability:

$$a_{\min} = X_{cp} - U_y \sigma; a_{\max} = X_{cp} + U_y \sigma,$$

where  $a_{\min}$  and  $a_{\max}$  — upper and lower limits, correspondingly, of the ‘Reference Hydrochemical Background’,  $X_{cp}$  — mean arithmetic deviation in the sample,  $\sigma$  — mean square deviation in the sample,  $U_y$  — coefficient of the normalized Laplace transform’s variable. For 95%



**Fig. 1. Heavy metals migration routes**

*Compiled by the authors*

confidence probability (conventionally used to define the hydrochemical background),  $U_y = 1.96$ . When the confidence probability rises to 99%,  $U_y = 2.58$  [8].

## 3. Findings and Discussion

### 3.1. The way of heavy metals spread

The causes and environmental impact of changing geochemical status of rivers and channels can be traced with the help of a model showing the migration routes of heavy metals contained in ferrosilicon shale rock of iron ore deposits (Fig. 1). With the current mining, transportation and waste storage techniques, HMs spread over vast territories carried with dust and waste waters and thus pollute the air, soil and alluvial aquifers. These geological components are tightly connected with surface watercourses, which, in fact, accumulate the contaminants. This environmental impact affects the ecosystems of the land and rivers [9, 10]. Heavy metals contaminate industrial and urban territories affecting in the long run people’s lives and health.

### 3.2. Zoning of the Oskol river on the basis of its natural features and human impact

Five areas have been identified in the river which have typical natural and technogenic features and on which sampling points were installed (Table 1).

Table 1. **Description of sampling points** (compiled by the authors)

Samp-ling point	Location	Technogenic features	Natural features
P1	3.5 km upstream from Staryi Oskol	No cities or industrial sites.	The river waters are of hydrocarbonate/calcium type; it has no big tributaries
P2	The mouth of the Oskolets river, a major tributary of the Oskol river with the basin of 540 km and the total length of 45 km	Main pollutants: Lebedinsky GOK, Stoilensky GOK and the city of Gubkin. The inflow of technogenic waters, which are mainly fed by waste waters, increases the mineralization of the river water	Cropout of the iron ore deposit
P3	1.5 km downstream from Staryi Oskol, 1 km downstream from the discharge point for the urban sewage waters	This is an impact zone of Oskol Electrometallurgical Plant and the city of Staryi Oskol	Discharge of a large aquifer; the iron ore deposit
P4	25 km downstream from Staryi Oskol, near the village of Ivanovka	There are no big industrial sites but the area has quite a vast agricultural infrastructure; an impact zone of villages and farms.	Cropout of the iron ore deposit
P5	47 km downstream from Staryi Oskol, near the town of Volokonovka	There are no cities, industrial sites or farms	Multiple tributaries carrying relatively clean waters inflowing in the Oskol river

### 3.3. Seasonal and spatial distribution of heavy metals in the Oskol river waters

**Table 2** shows spatial/seasonal concentrations of HMs in the Oskol river waters allowing for the reference hydrochemical background. In case of the lower reference hydrochemical background being in the negative range as determined through calculations, zero level would be taken for reference. The concentrations of the examined metals in the river waters are quite high and vary within

a broad range. A high concentration of Fe is observed in almost all samples.

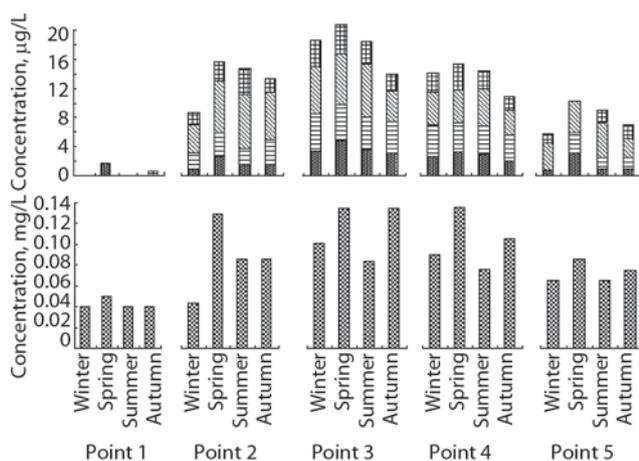
This can be attributed to the fact that ferruginous quartzites, which are cropping out in the basin area, are being washed away (**Fig. 2**). These ores are extremely rich in Fe (from 50 to 62.3%), with only a slight concentration of impurities (such as S, P, silica). A considerable portion of ores is surface mined, which aggravates the impact of mining and steel industries on the hydrochemical indicators.

Table 2. **Seasonal/spatial distribution of heavy metals in the Oskol river waters** (numerator — average value, denominator — standard deviation) (calculated by the authors)

HM, mcg/L	Winter	Spring	Summer	Autumn	Year average	Background**
<i>Sampling Point 1</i>						
Fe*	0.05/0.04	0.05/0.05	0.04/0.01	0.04/0.04	0.04/0.03	0.0–0.10 / 0.0–0.13
Cu	0/0	1.7/1.5	0/0	0/0	0.4/0.1	0.2–0.6 / 0.2–0.7
Zn	0/0	0/0	0/0	0/0	0/0	0 / 0
Ni	0/0	0/0	0/0	0/0	0/0	0 / 0
Cr	0/0	0/0	0/0	0.6/0.5	0.5/0.2	0.0–1.2 / 0.0–1.5
Pb	0.3/0.2	0.1/0.0	0.2/0.1	0.2/0.0	0.2/0.1	0.0–0.4 / 0.0–0.5
<i>Sampling Point 2</i>						
Fe*	0.05/0.04	0.12/0.07	0.08/0.05	0.08/0.07	0.08/0.05	0.0–0.18 / 0.0–0.20
Cu	1.5/0.9	2.5/0.5	1.4/1.2	1.3/1.2	1.5/1.2	0.0–3.9 / 0.0–4.6
Zn	2.0/1.8	3.0/1.2	2.0/1.7	3.2/0.7	2.6/1.4	0.0–5.3 / 0.0–6.2
Ni	3.5/3.1	6.6/0.5	6.9/1.2	6.0/0.4	5.8/2.0	1.9–9.7 / 0.6–10.9
Cr	1.7/1.5	2.4/0.9	3.3/0.4	1.8/1.8	2.2/1.3	0.0–4.7 / 0.0–5.6
Pb	0.4/0.2	0.2/0.1	0.2/0.1	0.3/0.2	0.3/0.1	0.0–0.5 / 0.0–0.63
<i>Sampling Point 3</i>						
Fe*	0.06/0.03	0.08/0.05	0.05/0.04	0.08/0.07	0.07/0.04	0.0–0.14 / 0.0–0.17
Cu	2.8/0.5	3.9/1.2	2.9/0.1	2.6/0.6	3.0/0.9	1.2–4.8 / 1.2–5.3
Zn	4.2/0.7	4.1/0.7	3.7/0.2	3.5/1.4	3.9/0.8	2.3–5.5 / 1.8–6.0
Ni	5.4/0.7	5.8/1.1	6.0/1.0	3.5/3.1	5.2/1.8	1.7–8.7 / 0.6–9.8
Cr	2.9/1.0	3.3/0.4	2.6/0.6	1.9/1.7	2.6/1.1	0.4–4.8 / 0.0–5.4
Pb	0.5/0.3	0.3/0.1	0.5/0.1	0.4/0.1	0.4/0.2	0.0–0. / 0.0–0.9
<i>Sampling Point 4</i>						
Fe*	0.06/0.01	0.09/0.04	0.05/0.02	0.07/0.01	0.07/0.03	0.01–0.13 / 0.0–0.15
Cu	2.8/0.5	3.3/1.3	3.0/0.6	2.1/0.1	2.8/1.0	0.8–4.8 / 0.2–5.4
Zn	3.6/0.6	3.8/0.4	3.6/0.9	3.3/0.5	3.6/0.7	2.2–5.0 / 1.8–5.4
Ni	4.2/0.5	4.1/0.6	4.8/1.4	3.3/2.9	4.2/1.9	1.0–7.9 / 0.7–9.1

<i>The finishing of Table 2</i>						
HM, mcg/L	Winter	Spring	Summer	Autumn	Year average	Background**
Cr	2.5/0.9	3.3/0.4	2.3/0.6	1.7/1.5	2.1/1.6	0.0–5.3 / 0.0–6.2
Pb	0.4/0.2	0.2/0.2	0.2/0.2	0.3/0.3	0.2/0.2	0.0–0.7 / 0.0–0.8
<i>Sampling Point 5</i>						
Fe*	0.08/0.06	0.08/0.06	0.02/0.01	0.07/0.07	0.07/0.06	0.0–0.20 / 0.0–0.24
Cu	1.4/1.0	3.2/1.4	1.6/1.1	1.6/1.1	1.8/1.5	0.0–4.7 / 0.0–5.7
Zn	0/0	2.5/1.2	2.1/1.5	2.1/1.5	1.5/1.3	0.0–4.2 / 0.0–5.2
Ni	3.5/2.0	4.1/1.8	4.5/1.8	2.5/3.5	3.9/2.7	0.0–9.2 / 0.0–10.9
Cr	1.1/1.6	0/0	2.1/1.5	1.6/0.6	1.4/0.9	0.0–3.6 / 0.0–4.5
Pb	0.1/0.1	0.1/0.0	0.2/0.0	0.1/0.1	0.1/0.1	0.0–0.2 / 0.0–0.2

\* Concentration of Fe in mg/L  
 \*\* Numerator and denominator — confidence probability p = 95 and 99%, correspondingly



**Fig. 2. Seasonal variations in the HM concentrations in different sampling points on the Oskol river:**  
 1 — Cu; 2 — Zn; 3 — Ni; 4 — Cr; 5 — Fe  
*Calculated by the authors*

A slightly higher HM background is observed in samples taken from P1. Slightly higher concentrations of Cr and Pb in the autumn may be attributed to contaminated rainfall and soil washouts.

Higher concentrations of all the components from Points 2 and 3 can be observed in the river waters. Rising concentrations are especially noticeable in the period of spring floods. And certain Cu parameters exceeding the background values go beyond the interval  $X_{cp} = +3\sigma$  ( $P = 99.73\%$ ), which indicates extremely high pollution. A drastic rise in the concentrations of such elements as Cu, Cr, Ni, Zn, Pb (which can exceed the background concentrations by up to 2 times) indicates that the metals entered the watercourse in the course of human activity. Steel production sites (including those for stainless steel) at Oskol Electrometallurgical Plant are the main source of HMs. The concentrations are also higher where sewage and industrial waste waters are discharged in the cities of Staryi Oskol and Gubkin. Besides, the contaminated pit waters tend to migrate from the settlers. The piles of contaminated soils accumulated around the production sites may serve as another source of HMs contaminating the ground and surface waters in the basin.

Further downstream, after the area where a number of tributaries carrying relatively clean waters flow in, the concentrations of HMs gradually decrease. A lower concentration of Fe registered downstream can be attributed to the fact that the river flows away from the ferruginous quartzite cropout zone, as well as from the area impacted by mining and steel industries. Sorption also plays an important role when it comes to removal of HMs from water. It is due to a high sorption potential of marly chalk sedimentary formations that are opened up by the riverbed. The riverbed is mainly built with fine limestone sand having a high absorption capacity ( $S:L = 1:10$ ): Zn — 10.02, Pb — 7.7, Cu — 1.04 g/t [11]. The sorption process goes quickly measured in minutes and hours (for Cu — around 10–15 minutes, for Zn — around 60 min). Saturation of the river waters with bicarbonate ions (the average value is 280 mg/L,  $\sigma = 22$ ) helps precipitate HMs in the form of insoluble hydroxo compounds [12]. Due to high concentrations of iron, heavy metals tend to accumulate in the suspended matter through bonding and forming hydroxo and aqua complexes of Fe, which then precipitate to form bottom sediments [11].

In spite of the favourable conditions for self-purification of the river waters, HMs get carried over long distances. Thus, high concentrations of Cu and Zn were observed in the Oskol river at the Ukrainian border (29.4 km to the mouth) in the sampling point situated 275 km downstream from the sources of pollution (Cu and Zn — 5 and 3 mcg/L, respectively).

Let's analyze the seasonal variations in the concentrations of HMs (see Fig. 2). A regular increase in the HM concentrations in the spring time is primarily due to their carry-over during the flood season. The same phenomenon would be true for Fe during the autumn rainy period. The HM concentrations are also quite high in the summer time, which can be explained by the impact of weakly acidic rainfalls as they are more frequent during the summer season.

It is a well-known fact that acid rains wash HMs out of soils and bottom sediments [13]. Besides, as the number of free ions increases at lower pH levels, the toxicity of HMs is higher in acid waters than in alkaline waters [14].

### 3.4. The impact of HM pollution on the low-water Oskol river

Low-water rivers and streams are more susceptible and have a low capacity for self-purification [7, 8, 15]. It is commonly believed that heavy metals have no biological function. At the same time, even small amounts of them can be toxic for most living creatures and plants [11, 16, 17]. Heavy metal ions are highly reactive and can spread over long distances carried away by watercourses; they have a high bioaccumulative potential and tend to accumulate in bottom sediments [13, 18, 19]. All this makes HMs especially hazardous for the ecosystems of the low-water Oskol river.

When heavy metals enter the low-water Oskol river, a whole series of hydrochemical interactions is triggered disrupting the natural biochemical and physico-chemical processes. Heavy metals interact with biotic and abiotic natural components. Some of the HMs are carried away from the entry point. Some of them accumulate in bottom sediments, aquatic vegetation, benthos, fish and river animals. Heavy metals may trigger numerous physical, chemical and biological changes.

Heavy metals can have both direct and indirect effect on aquatic ecosystems through disrupting the natural biochemical and physico-chemical processes. Heavy metals can often cause degradation or even a complete destruction of ecosystems. However, the most common reactions to heavy metals include the following: a poorer diversity of animal and plant species, their mutation, a poorer productive capacity. Heavy metals produce extremely diverse effects on aquatic plants. The key response to them, which includes a decreased diversity and population density, would be typical of the most polluted areas. Lower growth and reproducibility rates are among the most common effects produced by heavy metals on fish.

In the long run, the considerable toxic effect produced by heavy metals on low-water rivers affect people and their health.

Multiple sources of pollution in the region, their close location, heavy metals carried away with air streams and surface waters lead to a wide-scale pollution. Because of this, we cannot expect any real improvement in the years to come. On the contrary, a further increase in the man-caused pollution may lead to an environmental crisis.

### 4. Conclusions

The following conclusions can be drawn from the obtained findings:

1. The Oskol river is a typical low-water river highly susceptible to heavy metal pollution. With the current mining, transportation and waste storage techniques, HMs spread over vast territories carried with dust and waste waters and thus pollute rivers, which in fact accumulate the contaminants.

2. Taking into consideration the natural and human factors, the authors did zoning of the low-water river of

Oskol, which is exposed to a variety of impacts caused by iron ore deposits. The natural factors include a cropout of ferruginous quartzites, their weathering, washing and spread over long distances. The human factors are related to the mining and processing of iron ore, as well as the presence of single-industry cities.

3. The research shows that the river waters have high concentrations of heavy metals which vary within a broad range. A high concentration of Fe is attributed to the wash-out of ferruginous quartzites, which crop out in the river basin. The HM concentrations rise significantly in the areas of direct impact by the mining and steel companies and the single-industry cities. This indicates a considerable impact of man-caused pollution. In spite of clean waters from tributaries and ground waters, as well as a high absorption capacity of drainable rock, HMs get carried over long distances thus affecting the terrestrial and aquatic ecosystems. That is what makes the Oskol river highly susceptible and diminishes its self-purification ability.

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# ЧЕРНЫЕ металлы

## CHERNYE METALLY

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